A new He–CO interaction energy surface with vibrational coordinate dependence. I. Ab initio potential and infrared spectrum

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The intermolecular potential energy surface of the He–CO complex including the CO bond length dependence has been calculated using symmetry-adapted perturbation theory (SAPT). The potential has a minimum of $e_m = -23.734$ cm$^{-1}$ with $R_m = 6.53$ bohr at a skew geometry ($\theta_m = 48.4^\circ$) if the molecular bond length is fixed at the equilibrium value of 2.132 bohr. We have applied the potential in the calculation of bound state levels and the infrared spectrum for the $^3$He–CO and $^4$He–CO complexes. The computed $ab$ initio transition frequencies are found to agree within 0.1 cm$^{-1}$ with experiment. In paper II [J. P. Reid, H. M. Quiney, and C. J. S. M. Simpson, J. Chem. Phys. 107, 9929 (1997)], the potential surface is used to calculate vibrational relaxation cross sections and rate constants. © 1997 American Institute of Physics. [S0021-9606(97)03146-2]

I. INTRODUCTION

The interaction between the helium atom and the carbon monoxide molecule has been the subject of a variety of experimental and theoretical studies. The system is of interest from an astrophysical point of view on account of the role that the CO molecule plays in dense interstellar clouds. Carbon monoxide is excited mostly by collisions with abundant species such as He and H$_2$ in that environment. Additionally, the He–CO van der Waals complex shows interesting dynamics which lie between the semirigid and nearly free rotor limits.

The relatively small number of electrons of He–CO permits theoreticians to calculate intermolecular potential energy surfaces by $ab$ initio methods. Thomas, Kraemer, and Diercksen (TKD) published a potential in 1980$^1$ that was calculated at the singles and doubles configuration interaction (CISD) level. Although their potential was state-of-the-art at that time, the use of rather small basis sets resulted in an underestimated potential well depth. Furthermore, the interaction energy was not corrected for the basis set superposition error (BSSE). The TKD potential was extended later$^2$ to include the dependence on the CO bond length. More recently, two $ab$ initio potentials were computed by the supermolecular approach using fourth-order many-body perturbation theory (MBPT).$^3,4$ The authors of the current paper reported a preliminary potential calculated by applying symmetry-adapted perturbation theory (SAPT).$^5$

A number of spectroscopic studies as well have been devoted to the He–CO complex. Chuaqui et al.$^6$ recorded high-resolution infrared spectra near the fundamental band region of the CO monomer for the complex with $^3$He and $^4$He. A more powerful spectroscopic technique was applied recently$^7$ to detect the “hidden” lines in the spectra, which were obscured by transitions of the CO monomer in the original measurements. The authors of Ref. 6 could not assign all observed transitions using conventional spectroscopic methods and theoretical spectra generated from the $ab$ initio TKD potential. Therefore, a two-dimensional potential energy surface named $V_{1(3,3)}$ was fitted to reproduce the experimental transition frequencies. Subsequently, a potential with a different functional form was determined from a fit to the same set of spectroscopic data.$^8$ The starting point of the new potential surface was the exchange-Coulomb (XC) model potential, which is partly based on $ab$ initio information on the exchange-repulsion energy and long-range induction and dispersion coefficients. This “XC” potential reproduced the observed spectrum as well as the $V_{1(3,3)}$ potential. Moreover, because of its sounder theoretical basis the XC potential is expected to be more realistic in the regions not sampled by the spectroscopic data.

The semi-empirical XC and $V_{1(3,3)}$ potentials and the $ab$ initio TKD and SAPT potentials were used to calculate pressure broadening and shifting cross sections for pure rotational transitions of CO in helium.$^9$ Good qualitative agreement was obtained for the cross sections computed from the XC, $V_{1(3,3)}$, and SAPT potentials. The theoretical data, however, are in substantial disagreement with experiment$^{10}$ at very low temperatures. This deviation is probably due to experimental errors or the breakdown of the line-shape theory, not because of inaccuracies in the potentials. The agreement of the cross sections obtained from the TKD potential with some of the experimental very low temperature data appeared to be fortuitous. Second virial coefficients computed from the SAPT potential$^5$ and from the XC and $V_{1(3,3)}$ potentials$^{11}$ were in reasonable accord with experi-
mental data. The SAPT potential was also tested against experimental transport properties. \(^1\!\!2\)

Vibrational relaxation of CO (\(v = 1\)) by inelastic collisions with helium atoms has been the subject of various theoretical studies (see paper II\(^1\!\!3\) and references therein). Vibrational relaxation strongly depends on the shape of the intermolecular potential. Rate constants determined at very low temperatures are sensitive to the van der Waals well, while the anisotropy of the repulsive wall is probed at higher temperatures. Most of the studies on vibrational relaxation rate constants of the last decade used the TKD potential. \(^1\!\!2\)

Since comparative studies have shown that this TKD potential suffers from inaccuracies, a high quality He–CO potential including the vibrational coordinate dependence is needed.

The current paper presents the calculation of an ab initio SAPT potential dependent on the CO bond length. In Ref. 5, the two-dimensional SAPT potential was used in dynamical calculations on the frequencies and intensities of the transitions in the infrared spectrum accompanying the fundamental bond of CO. It was found that the line positions agreed within a few tenths of a wave number with the experimental data from Ref. 6. To test the accuracy of the current three-dimensional potential in the region of the Van der Waals minimum a new series of dynamical calculations have been performed. The results are compared with the data from Ref. 6 as well as with the new data from Ref. 7. In the subsequent article (paper II), the three-dimensional potential is used to calculate rate constants for the vibrational relaxation of the \(^4\)He–CO and \(^3\)He–CO complexes.

II. OUTLINE OF SAPT CALCULATIONS

The SAPT approach used here has been described in a number of papers. \(^5\!\!4\!\!\!–10\) The interaction energy can be decomposed into terms corresponding to the Hartree–Fock (\(E\)\(_{\text{HF}}\)) and correlated (\(E\)\(_{\text{corr}}\)) levels of theory,

\[
E_{\text{int}} = E_{\text{HF}} + E_{\text{corr}}.
\]

The Hartree–Fock interaction energy was obtained from supermolecular self-consistent field calculations and represented as a sum of individual contributions. \(^17\!\!–20\) The SAPT contribution to the interaction energy at the correlated level is represented here as in Ref. 5, except that the electron correlation effects on the exact first-order exchange contribution are approximated by

\[
\epsilon_{\text{exch}}^{(1)} = \epsilon_{\text{exch}}^{(1)} + \epsilon_{\text{exch}}^{(2)} + \Delta_{\text{exch}}^{(1)} \quad \text{(CCSD)}.
\]

In the expression for \(E_{\text{exch}}^{(2)}\) the first- and second-order cluster operators are replaced by converged coupled-cluster operators, \(^21\) leading to a sum of higher-order terms (in the intramolecular correlation) denoted \(\Delta_{\text{exch}}^{(1)}\) (CCSD). Although the CCSD correction was not included in the potential of Ref. 5, it was discussed that it may have a non-negligible effect on the anisotropy.

The interaction energy surface for the He–CO system can be naturally expressed in Jacobi coordinates \((R, r, \theta)\), where \(R\) is the distance between the c.m. of CO and the helium atom, \(r\) is the CO bond length, and \(\theta\) is the angle between the vector pointing from the molecular c.m. to the atom and the vector pointing from the carbon to the oxygen nucleus. Calculations have been performed for intermolecular distances \(R = 5, 6, 7, 8,\) and 10 bohr, and seven equivalent \(\theta\) ranging from \(\theta = 0^\circ\) to \(\theta = 180^\circ\). In addition, potential energy curves have been computed for \(\theta = 15^\circ\), \(75^\circ\), \(105^\circ\), and \(165^\circ\). The CO bond length \(r\) was varied over five values: the equilibrium bond length \(r_e = 1.232\) bohr, \(^22\) the two values of \(r = 1.898\) and 2.234 bohr at which Schinke and Diercksen \(^23\) previously calculated a potential energy surface, and two additional values of \(r = 2.050\) and 2.170 bohr. In total, we calculated 275 points on the three-dimensional surface.

As in our previous work, \(^2\) a \([5s3p2d]\) basis was used for the helium atom. The \(s\) orbitals were represented by the \((61111)\) contraction of van Duijneveldt’s 10s set, \(^24\) and the exponents of the polarization functions were taken from Ref. 24. For the carbon and oxygen atoms we took the \([8s5p3d1f]\) basis sets of Diercksen and Sadlej, \(^25\) optimized for the dipole and quadrupole properties of the CO molecule. In Ref. 5, however, the five steepest \(p\) functions on both C and O were inadvertently contracted to one basis function instead of two. All terms except \(E_{\text{disp}}^{(2)}\) were calculated with this basis set. In the calculation of \(E_{\text{disp}}\) an extended basis set was used with diffuse bond functions from Ref. 26, located at the middle of the intermolecular bond. To investigate the effect of the basis, we performed additional calculations at \(R = 7\) bohr, \(r = 2.132\) bohr, and \(\theta = 0^\circ\) and \(180^\circ\) with the \([9s7p3d2f]\) basis sets for the carbon and oxygen atoms from Hettema et al. \(^26\) Polarization functions were applied in their spherical form (five \(d\) functions and seven \(f\) functions). Full dimer basis sets were used in the SAPT calculations in order to account for charge-overlap effects.

All calculations were performed employing the SAPT system of codes. \(^28\) The POCOR package was used to compute additional long-range induction and dispersion coefficients corresponding to the multipole expanded induction and dispersion energies. These long-range coefficients, calculated with the same basis sets and at the same level of theory, were subsequently used in the analytical fitting of the induction and dispersion energies. The Boys–Bernardi counterpoise correction \(^30\) was applied to eliminate the BSSE from the supermolecular Hartree–Fock interaction energy.

A two-step procedure was used in fitting the interaction energy. In the first step, one-dimensional fits in \(R\) were produced for each value of \(\theta\); subsequently we expanded all fit parameters in Legendre polynomials \(P_l(\cos \theta)\). The CO bond length dependence of the potential was represented by expanding the linear parameters in powers of \((r-r_e)/2.132\) bohr. In the second step, we used a global three-dimensional fitting procedure with the parameters from the one-dimensional fits of the first step as starting point. The fitted potential reproduces all ab initio calculated points within 2%. In the region of the potential minimum the difference between the fitted potential energy and its ab initio counterpart is typically a few tenths of a wave number and at
FIG. 1. Contour plot of the ab initio potential (in cm$^{-1}$) at $r = 2.132$ bohr.

dimensional potential is available from the authors at the electronic mail address avda@theochem.kun.nl.

III. FEATURES OF THE POTENTIAL ENERGY SURFACE

We first look at the potential energy surface, fitted to the ab initio calculated data points, for $r$ fixed at the experimental CO equilibrium bond length $r_e = 2.132$ bohr. The potential surface shows a single minimum of depth $\epsilon_m = -23.734$ cm$^{-1}$ at $R_m = 6.53$ bohr and $\vartheta_m = 48.4^\circ$. Comparison with the previously published two-dimensional potential energy surface$^3$ shows that the current potential predicts a minimum corresponding to the skew symmetry of the complex instead of the linear CO–He configuration. As the potential is very flat in region $\vartheta = 0^\circ$ to $120^\circ$, small inaccuracies in the basis set or the fit can cause the global minimum to shift from one geometry to the other. For the $\vartheta = 0^\circ$ curve at $r = 2.132$ bohr, the potential shows a minimal value at $R = 6.94$ bohr of $\epsilon = -21.078$ cm$^{-1}$, which is only a few wave numbers above the global minimum. The improvement of the basis set, compared to Ref. 5, has a significant effect on the interaction energies. Two recently computed MBPT4 potentials predict global minima of $\epsilon = -20.32$ cm$^{-1}$ at $\vartheta = 60^\circ$, $R_m = 6.60$ bohr$^4$ and $\epsilon_m = -21.95$ cm$^{-1}$ at $\vartheta = 70^\circ$, $R_m = 6.43$, bohr$^3$, i.e., at the skew geometry. By contrast, a linear equilibrium geometry with $\epsilon_m = -22.531$ cm$^{-1}$, $R_m = 6.84$ bohr was predicted by the ‘‘XC’’ model potential,$^8$ which was fitted to the infrared spectrum and was based on an exchange-Coulomb model. How difficult it is to locate the global minimum is illustrated by the fact that the older $V_{3(3,3)}$ potential fitted to the same spectroscopic data has its minimum at the skew geometry.$^6$ These ab initio and semi-empirical potential surfaces were compared in a recent work by Thachuk et al.$^9$, together with our two-dimensional potential. Agreement between the current potential and the semi-empirical XC potential, which has proved to be very accu-

**TABLE I.** Components of the interaction energy at $R = 7$ bohr, $r = 2.132$ bohr computed in a basis with [8s5p3d1f] functions on C and O and additional bond functions for $E_{\text{disp}}^{(2)}$ (A) and a basis with [9s7p3d2f] functions on C and O and no bond functions (B).

<table>
<thead>
<tr>
<th>$\vartheta = 0^\circ$</th>
<th>$\vartheta = 180^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>$\theta$</td>
</tr>
<tr>
<td>basis A</td>
<td>basis B</td>
</tr>
<tr>
<td>$E_{\text{int}}$</td>
<td>$E_{\text{int}}$</td>
</tr>
<tr>
<td>$E_{\text{exchange}} + \Delta_{\text{exch}}^{(1)}$ (CCSD)</td>
<td>$E_{\text{exchange}} + \Delta_{\text{exch}}^{(1)}$ (CCSD)</td>
</tr>
<tr>
<td>$E_{\text{disp}}$</td>
<td>$E_{\text{disp}}$</td>
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<tr>
<td>$E_{\text{disp}}^{(2)}$</td>
<td>$E_{\text{disp}}^{(2)}$</td>
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<tr>
<td>$E_{\text{disp}}^{(2)}$</td>
<td>$E_{\text{disp}}^{(2)}$</td>
</tr>
<tr>
<td>$E_{\text{int}}$</td>
<td>$E_{\text{int}}$</td>
</tr>
</tbody>
</table>

rate, is better than for our old potential surface and is now within 2 cm$^{-1}$. Figure 1 depicts a contour plot of the ab initio potential at $r = 2.132$ bohr.

In Table I we compare the separate components of the interaction energy computed in two different basis sets. In case A, all components were computed with the basis sets from Diercksen and Sadlej$^2$ for the C and O atoms, except for the contribution $E_{\text{disp}}^{(2)}$ which was calculated in the basis set with additional bond functions. The basis sets from Hettema et al.$^{27}$ for C and O were used in case B, where no bond functions were included (cf., Sec. II). From Table I it is seen that the differences between the two basis sets are manifest in two components, namely, the intramolecular correlation correction to the first-order exchange energy, $E_{\text{exchange}}^{(1)} + \Delta_{\text{exchange}}^{(1)}$ (CCSD), and the dispersion energy $E_{\text{disp}}^{(2)}$. Since basis B contains more $s$ and $p$ functions on the CO monomer, the intramolecular correlation is taken into account to a greater extent than in basis A. It is known that molecules with triple bonds are sensitive to electronic correlation in higher-order levels of perturbation theory.$^{31}$ This explains the difference in $E_{\text{exchange}}^{(1)} + \Delta_{\text{exchange}}^{(1)}$ (CCSD), which is as large as 26% for $\vartheta = 180^\circ$. In comparison with the results from Ref. 5 we observe that at $\vartheta = 0^\circ$ and $180^\circ$ the Hartree–Fock interaction energies are 0.83 and 6.50 cm$^{-1}$ higher, respectively, while $E_{\text{exchange}}^{(1)} + \Delta_{\text{exchange}}^{(1)}$ (CCSD) at $\vartheta = 0^\circ$ is 1.50 cm$^{-1}$ higher. These deviations are caused by the incorrect contraction of the steepest $p$ functions in Ref. 5. Second, in basis A, which includes bond functions in the calculation of $E_{\text{disp}}^{(2)}$, the dispersion energy $E_{\text{disp}}^{(2)}$ is 1.3 and 5.7 cm$^{-1}$ lower at $\vartheta = 0^\circ$ and 180$^\circ$, respectively, in comparison with basis B (without bond functions). The results for basis B are approximately equal to the results found for $E_{\text{disp}}^{(2)}$ in Ref.5: $-38.81$ and $-94.48$ cm$^{-1}$ at $\vartheta = 0^\circ$ and 180$^\circ$, respectively. Although the calculation of $E_{\text{disp}}^{(2)}$ is not strictly variational, it follows in practice

**TABLE II.** Expectation values in atomic units of $(r - r_e)^k$, $k = 1, 2, 3$, for the $\nu = 0$ and $\nu = 1$ vibrational states.

<table>
<thead>
<tr>
<th>$\nu = 0$</th>
<th>$\nu = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(r - r_e)$</td>
<td>0.0074502</td>
</tr>
<tr>
<td>$(r - r_e)^2$</td>
<td>0.0041377</td>
</tr>
<tr>
<td>$(r - r_e)^3$</td>
<td>0.0001120</td>
</tr>
</tbody>
</table>
that an improvement of the basis implies a lowering of $E^{(20)}_{\text{disp}}$.

If only nucleus-centered basis sets are used, functions with high angular momenta have to be included to describe the dispersion energy properly. This can be avoided by extending the basis set with a series of diffuse bond functions with low angular quantum numbers. The exact origin and exponents of the bond functions hardly affect the energy. As $E^{(20)}_{\text{disp}}$ constitutes the main contribution to the dispersion energy, calculating this term (at relatively low cost) in a basis with extensions of the bond functions hardly affects the energy. As the van der Waals complexes can be described in a set of coordinates relative to either a space-fixed or a dimer-embedded frame.3 2 the space-fixed coordinate system. It is this description that the potential function can then be replaced by their vibrationally averaged counterparts.

IV. BOUND STATES AND INFRARED SPECTRUM OF He–CO

As is well known, nuclear motions of weakly bound van der Waals complexes can be described in a set of coordinates relative to either a space-fixed or a dimer-embedded frame.32 When the strength of the anisotropy in the intermolecular potential is small in comparison with the end-over-end rotational constant $1/(2\mu R^3)$ of the dimer, it is convenient to use the space-fixed coordinate system. It is this description that is used here even though the anisotropy of the potential in the van der Waals region is not particularly weak. We did this because the energy levels and infrared transitions of the He–CO complex can be approximately classified by the case $(a)$ coupling of Bratoz and Martin33 (see Refs. 32 and 34 for a review). Furthermore, the intramolecular vibration can to a good approximation be decoupled from the intermolecular modes because of the high frequency ($\sim 2143$ cm$^{-1}$) of the former. The $r$-dependent rotational constant of CO and potential function can then be replaced by their vibrationally averaged counterparts, $b_v$ and $V_v(R, \theta)$, respectively, with $v$ labeling the intramolecular vibrational mode. The nuclear motions of He–CO are thus described by the Hamiltonian

\[
H_v = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} + \frac{l^2}{2\mu R^2} + b_v j^2 + V_v(R, \theta),
\]

where $\mu$ is the reduced mass of the complex and $j$ and $l$ are the angular momenta associated with the molecular rotation and with the end-over-end rotation of the system, respectively. Most calculations in this work applied this adiabatic decoupling approximation. Additional full three-dimensional $(R, \theta, r)$ dynamical computations were performed for the $J=0$ and $1$ states of $^4\text{He–CO}$. In these calculations, the ground state potential for the CO molecule from Huxley and Murrell35 was added to the intermolecular potential function.

In case of an isotropic potential, $j$ and $l$ are good quantum numbers, corresponding to the molecular rotation in the complex and the end-over-end rotation of $R$, respectively. The total angular momentum $J=j+l$ is always conserved but a degenerate $(j,l)$-level splits into sublevels $J=|j-l|, \ldots, j+l$ under the influence of the anisotropy of the potential. It was shown in our previous paper3 that for most of the eigenstates, the dominant $(j,l)$ contribution to the wave function is of the order of 90%, suggesting that the CO molecule in the dimer behaves like a slightly hindered rotor. This was confirmed by the observation that although most transitions did not obey selection rules corresponding to the case $(a)$ coupling of Bratoz and Martin,33 the most intense lines did correspond to the free internal rotor limit. Therefore, the states can to be labeled a good approximation by $j$ and $l$.

When we assume that the CO vibration is decoupled from the intermolecular modes, the transition frequencies are given by

\[
u(v=1,j^*,l^*;J^*,J^*+v=0,j^*,l^*,J^*) = E_j^{j^*} - E_j^{j^*,l^*,v=0} + Q(0),
\]

where $Q(0)=2143.2712$ cm$^{-1}$ is the frequency of the CO fundamental stretching mode, determined from a Dunham analysis.36 The intensities of the infrared transitions in He–CO accompanying the fundamental band of CO were calculated as in Ref. 5, at a temperature of $T=50$ K. The intermolecular transitions obey the following selection rules: $|\Delta J|=1$ with $(-1)^{j^*}(1)^{j^*+1}$, and $|\Delta J|=0$ or 1. In addition, the selection rules $\Delta l=0$ and $|\Delta j|=1$ hold approximately since $j$ and $l$ are nearly good quantum numbers.

To compute the vibrationally averaged potential surface $V_v(R, \theta)$ for a given vibrational state $v$ of the CO monomer, the powers $(r-r_j)^k$ in the analytical expression of the potential energy were replaced by their corresponding expectation values. We have determined the eigenfunctions of the potential from Ref. 35 by using the discrete variable representation (DVR) method with a basis of sinc functions.37 The expectation values of the powers of $(r-r_j)$ over the $v=0$ and $v=1$ vibrational states that were obtained from these eigenfunctions are listed in Table II.

A radial basis of Morse type oscillator functions38 was used for the $R$ coordinate. The parameters $R_c$, $D_c$, and $\omega_0$ were optimized by minimizing the energy of the $J=0$ state. This gave $R_c=13.050$ and $14.149$ bohr for $^4\text{He–CO}$ and $^6\text{He–CO}$.
The full three-dimensional calculations for a Morse type basis for the vibrational ground state of the CO molecule were fixed at 1.922 5125 and 1.905 0074 cm⁻¹, respectively. The rotational constant for the vibra-

tional ground state is close to the highly accurate value of 2 142.95 cm⁻¹, and order 10.020.

In Table III we summarize the results of the bound state calculations for ¹²C—12 amu, and ¹⁶O—15.994 91 amu. For practical reasons, all calculations were performed by the TRIATOM package, which uses the dimer-embedded frame, rather than by the ATDIATSF package, which is based on a space-fixed coordinate system. Note that both descriptions give exactly the same results, only the approximate quantum numbers labeling the states are different.

1³He—CO, respectively, Dₜ = 14.3758 cm⁻¹, and ωₜ = 9.9861 cm⁻¹. The final basis was restricted to the space with j = 10 for the angular basis and order n = 23 for the radial basis. The vibrationally averaged rotational constants b₀ and b₁ of the CO molecule were fixed at 1.922 5125 and 1.905 0074 cm⁻¹, respectively. The rotational constant for the vibrational ground state is close to the highly accurate value of 2 142.95 cm⁻¹ reported by Varberg and Evenson. In the full three-dimensional calculations a Morse type basis for r was used with r₀ = 2.1597 bohr, Dₜ = 82 303.0 cm⁻¹, ωₜ = 2142.95 cm⁻¹, and order n = 4. We used the following masses: ³He = 3.01603 amu, ⁴He = 4.002 60 amu, ¹²C = 12 amu, and ¹⁶O = 15.994 91 amu. For practical reasons, all calculations were performed by the TRIATOM package, which uses the dimer-embedded frame, rather than by the ATDIATSF package, which is based on a space-fixed coordinate system. Note that both descriptions give exactly the same results, only the approximate quantum numbers labeling the states are different.

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TABLE V. Energy levels (in cm\(^{-1}\)) of the \(^4\)He-CO complex, relative to the \((J,j,l)=(0,0,0)\) level at \(-5.5416\) and \(-5.5858\) cm\(^{-1}\) (theoretical values) for \(v=0\) and \(v=1\), respectively. "Experimental" values are from Ref. 7.

\[
\begin{array}{cccccc}
J & (j,l) & \text{This work} & \text{"Experimental"} & \text{This work} & \text{"Experimental"} \\
\hline
0 & (0,0) & 0.0 & 0.0 & 0.0 & 0.0 \\
 & (1,1) & 5.2131 & 5.1800 & 5.1781 & 5.1629 \\
1 & (0,1) & 0.7069 & 0.7022 & 0.7086 & 0.7000 \\
 & (1,0) & 3.9915 & 3.9771 & 3.9640 & 3.9404 \\
 & (1,1) & 4.4226 & 4.3869 & 4.3990 & 4.3517 \\
2 & (0,2) & 2.0968 & 2.0766 & 2.0961 & 2.0721 \\
 & (1,1) & 4.8145 & 4.8031 & 4.7846 & 4.7673 \\
 & (1,2) & 5.8609 & 5.8087 & 5.8371 & 5.7744 \\
3 & (0,3) & 4.1108 & 4.0626 & 4.1106 & 4.0590 \\
 & (1,3) & 7.9367 & - & 7.9133 & 7.8232 \\
\end{array}
\]

\(^{a}\)This level has not been directly observed; it is estimated to be at 7.856 cm\(^{-1}\).

The potential energy surface does not support states excited in the van der Waals stretch. It should be noted that states of positive energy lying below the \(j=1\) rotational level of the CO monomer are truly bound if they have parity \(p=\pm 1\). These states cannot mix with \(j=0\) continuum states, which have parity \(p=\mp 1\), since both \(p\) and \(J\) are conserved. The \(j=1\) rotational level of CO in its ground state was experimentally determined at 3.8450 cm\(^{-1}\). The ground state of \(^4\)He-CO is bound by 6.788 cm\(^{-1}\). Our earlier two-dimensional SAPT potential\(^{a}\) supports a ground state lying 0.174 cm\(^{-1}\) lower, which is in agreement with the observation that the old potential has a slightly deeper well. The "experimental" energy level scheme

 TABLE VI. Frequencies \(v\) (in cm\(^{-1}\)) and intensities (in arbitrary units, relative to the \((2,1,1)-(0,0,1)\) intensity) of the transitions in the infrared spectrum of \(^4\)He-CO accompanying the fundamental band of CO.

\[
\begin{array}{cccccc}
\text{Transition} & \text{This work} & \text{Observed, Ref. 6} & \\
(J\',J\',l\',J\',l\',l\') & \nu_{\text{calc}} & \text{Intensity} & \nu_{\text{calc}} & \text{Intensity} & \nu_{\text{calc}} - \nu_{\text{obs}} \\
\hline
(1,0,1)-(0,0,0) & 2143.9335 & 6.3 & 2143.9489 & 9 & -0.015 \\
(1,0,1)-(1,1,1) & 2138.7204 & 12.7 & 2138.7701 & 8 & -0.050 \\
(2,1,1)-(1,0,1) & 2147.3047 & 100.0 & 2147.3152 & 100 & -0.010 \\
(2,0,2)-(1,0,1) & 2144.6162 & 12.4 & 2144.6192 & 11 & -0.003 \\
(3,1,1)-(2,0,2) & 2145.2407 & 17.0 & 2145.2323 & 15 & 0.008 \\
(0,0,0)-(1,0,1) & 2147.6981 & 14.8 & 2147.7105 & 8 & -0.012 \\
(0,0,0)-(1,1,1) & 2142.5201 & 6.1 & 2142.5489 & 6 & -0.029 \\
(0,0,0)-(2,1,1) & 2141.8367 & 11.7 & 2141.8728 & 11 & -0.036 \\
(0,0,0)-(2,1,2) & 2139.1190 & 88.5 & 2139.1471 & 95 & -0.028 \\
(2,0,2)-(3,0,3) & 2141.2123 & 15.6 & 2141.2593 & 15 & -0.047 \\
(2,1,1)-(2,1,1) & 2144.2495 & 5.3 & 2144.2203 & 5 & 0.029 \\
(2,1,1)-(2,1,2) & 2142.1507 & 5.4 & 2142.2080 & 6 & -0.057 \\
\end{array}
\]

\(^{a}\)This line has not been observed.
shown in Table III was reported by Chan and McKellar\(^7\) who slightly modified the levels from Chuaqui et al.\(^6\) by including
the transition frequencies of the hidden lines. Furthermore, their scheme includes the \((J,j,l) = (4,1,4)\) level.

Full three-dimensional calculations for \(^4\)He–CO \((J = 0\) and \(1)\) showed that the bound levels are affected by less than
0.001 \(\text{cm}^{-1}\) by the decoupling approximation. For instance, the \((J,j,l) = (1,1,1)\) state for \(v = 0\) is decreased from 4.3083
to 4.3079 \(\text{cm}^{-1}\) by this approximation, while the
\((J,j,l) = (0,1,1)\) state for \(v = 1\) is increased from 5.3086 to
5.3087 \(\text{cm}^{-1}\). This is in agreement with the result found for
the He–HF complex\(^8\) that the coupling between inter- and
intramolecular modes is very small for atom–diatom systems.

The calculated infrared transition frequencies and intensities for the \(^3\)He–CO complex are reported in Table IV and
graphically illustrated in Fig. 2. Table IV shows that the
agreement of theoretical transition frequencies with the results of the high-resolution measurements\(^6,7\) is excellent. All line
positions agree within 0.1 \(\text{cm}^{-1}\) or better, while the rms.
deviation is 0.038 \(\text{cm}^{-1}\). The absolute errors of the transition
frequencies computed from our previous two-dimensional \textit{ab initio} potential\(^5\) were as large as 0.5 \(\text{cm}^{-1}\) for some transitions.
Only after scaling the short-range contribution to the
\(V_{3}(R)\) component of the potential energy agreement within
0.2 \(\text{cm}^{-1}\) for all transitions was reached, whereas the agreement we obtain now is twice as good without any scaling.
The transition intensities predicted by the \textit{ab initio} potential
also agree reasonably well with the experimental values. One
should keep in mind that intensities are determined from experiment with much less accuracy than the corresponding transition frequencies.\(^6\)

In Table V we report the bound state levels for the
\(^3\)He–CO complex generated from the \textit{ab initio} potential. The 12 transitions observed in Ref. 6 for \(^3\)He–CO were unsufficient
to determine the energy levels accurately. The addition of seven new transitions, however, enabled the authors of Ref. 7 to construct the experimental energy level scheme listed in Table V. The experimental \((J,j,l) = (3,1,3)\) level is absent since the \((3,0,3) - (3,1,3)\) transition could not be observed. Table VI and Fig. 3 show the \textit{ab initio} transition
frequencies and intensities for the \(^3\)He–CO complex, together
with their experimental counterparts from Refs. 6 and 7.
Agreement with experiment is equally good as for
\(^4\)He–CO. All line positions are reproduced within 0.06
\(\text{cm}^{-1}\); the rms. deviation is 0.033 \(\text{cm}^{-1}\). The infrared intensities are also correctly predicted. The excellent agreement
between theoretical and experimental transition frequencies for both \(^4\)He–CO and \(^3\)He–CO confirms that the \textit{ab initio}
calculated potential energy surface represents the anisotropy of the potential in the region of the van der Waals minimum
very accurately.

The band origin of the \(v = 1 - 0\) transition is lower in the He–CO complex than in the free monomer. The observed red shifts for \(^4\)He–CO and \(^3\)He–CO are \(-0.024\) and \(-0.021\) \(\text{cm}^{-1}\), respectively.\(^7\) the theoretical values are \(-0.048\) and \(-0.044\) \(\text{cm}^{-1}\), respectively. This overestimation of the red shifts is reflected in the mean difference between

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Comparison of theoretical and experimental infrared spectra of the \(^3\)He–CO complex accompanying the fundamental band of CO. The temperature is 50 K.}
\end{figure}

calculated and observed transition frequencies which are
\(-0.019\) and \(-0.017\) \(\text{cm}^{-1}\), respectively. As discussed
above, the bound state levels obtained from three-
dimensional and decoupled two-dimensional calculations
agree within 0.001 \(\text{cm}^{-1}\). The same result was found for the band origin. Therefore, we conclude that the remaining small
disagreements between theoretical and experimental red shifts must be due to minor inaccuracies in the potential function, rather than to the decoupling approximation.

\section*{V. SUMMARY AND CONCLUSIONS}

The interaction potential energy surface of the He–CO complex was calculated for a broad range of configurations using symmetry-adapted perturbation theory. In comparison with previous work\(^5\) the anisotropy of the exchange-repulsion energy was computed by the more advanced SAPT–CCSD method, the basis set was improved, and the CO bond length was varied over five values, which yields a full three-dimensional potential surface. We have shown that the present potential agrees very well with the accurate semi-empirical XC potential of Le Roy \textit{et al.}\(^8\) better than our earlier \textit{ab initio} potential.

Using the computed potential energy surface we have calculated bound rovibrational states and the infrared spectrum of the He–CO complex corresponding to the simultaneous excitation of the vibration and hindered rotation of the CO molecule within the dimer. Variational characterization of the rovibrational states revealed a ground state of
\(^4\)He–CO with a dissociation energy of 6.79 \(\text{cm}^{-1}\) and several angularly excited states of the complex. The predicted positions and intensities of lines in the infrared spectrum are in excellent agreement with the experimental spectrum.\(^6,7\)
The good agreement for the transition frequencies shows that the anisotropy of the potential in the well region is correct. The present \textit{ab initio} SAPT potential was used in the calculation of second virial coefficients.\textsuperscript{44} Very good agreement with the majority of available experimental data was obtained, showing that the potential well depth is also predicted correctly. In the companion paper II,\textsuperscript{13} the accuracy of the potential well depth and the correctness of its vibrational coordinate dependence is tested.

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